Production of Amorphous Alloy Balloons by Utilizing Viscous Flowability

Production of Amorphous Alloy Balloons by Utilizing Viscous Flowability*

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Synopsis

This paper deals with the first example for the production of an amorphous alloy balloon with a height of 30 mm by blowing at 510 K an amorphous $La_{55}Al_{25}Ni_{20}$ disk with a diameter of 35 mm and a thickness of 2.2 mm prepared by a metallic mold casting process. The blowing deformation utilizes the significant viscous flowability in the supercooled liquid region obtained by the transition from the amorphous solid. The key point which enables the blowing deformation is attributed to the finding that the La-Al-Ni amorphous alloy has a wide supercooled liquid region reaching 70 K before crystallization and has a high thermal stability against crystallization even in very low viscous state ranging from 10^6 to 10^7 Pa.s.

I. Introduction

Amorphous alloys have been produced by various methods such as liquid quenching, vapor condensation, solid-state reaction, chemical reduction,etc. Among these methods, the liquid quenching is the most popular method and the cooling rate is known to reach 10^5 to 10^6 K/s[1]. The cooling rate is almost equivalent to the critical cooling rate for formation of Fe-, Co- and Ni-based amorphous alloys. In order to achieve such a high cooling rate, the sample is required to have a thin thickness and hence the morphology of amorphous alloys without subsequent working is limited to a thin form.

Recently, the present authors have found new amorphous alloys with large glass-forming ability in La-[2], Mg-[3] and Zr-[4] base systems and clarified that amorphous cylinders with a diameter of 7 mm are formed by a metallic mold casting process with a cooling rate of

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several hundreds K/s. It has thus been demonstrated[5] that an amorphous alloy is produced by the conventional casting method as similar for conventional crystalline alloys. These new amorphous alloys have a wide supercooled liquid region in the temperature range below crystallization temperature (T_x) and can be easily deformed even by small applied load in the supercooled liquid region. This paper is intended to present the data on the formation of amorphous alloy balloons by utilizing the large deformability in the supercooled liquid.

II. Supercooled Liquid and Amorphous Phase

An amorphous alloy has a high mechanical strength at room temperature. However, the rise of temperature to the supercooled liquid region above the glass transition temperature (T_g) causes a significant softening of the amorphous alloy through a rapid decrease in viscosity. Here, we explain the feature of the supercooled liquid.

When an alloy with glass-forming ability is quenched rapidly from a liquid state, the liquidus phase changes to a solidus phase with a random atomic configuration which is nearly the same as that of the liquidus phase at a critical temperature, in the case where the cooling rate is large enough to suppress the nucleation and growth of a crystalline phase in the supercooled liquid region. Th critical temperature at which the supercooled liquid changes into the disordered solidus phase is defined as the glass-transition temperature and the nonequilibrium state is called as a glassy state or an amorphous state.

Figure 1 shows a schematic diagram illustrating the changes in the specific volume and atomic configuration by the phase transition among crystal, liquid, supercooled liquid and glass. The volume decreases significantly upon crystallization at the melting temperature (T_m), while that of the supercooled liquid decreases continuously along the line extrapolated from the volume of the liquidus phase with decreasing temperature. This is induced because of the decrease in the free volume in the supercooled liquid with decreasing temperature. At T_g, the freedom for the atomic movement in the supercooled liquid is lost, leading to the formation of a solidus phase containing an extra free volume. On the other hand, when the amorphous solid is heated, it changes to a crystalline phase through the glass transition.

As shown in Fig. 1, the glass transition corresponds to the change from an amorphous solid to a supercooled liquid and the

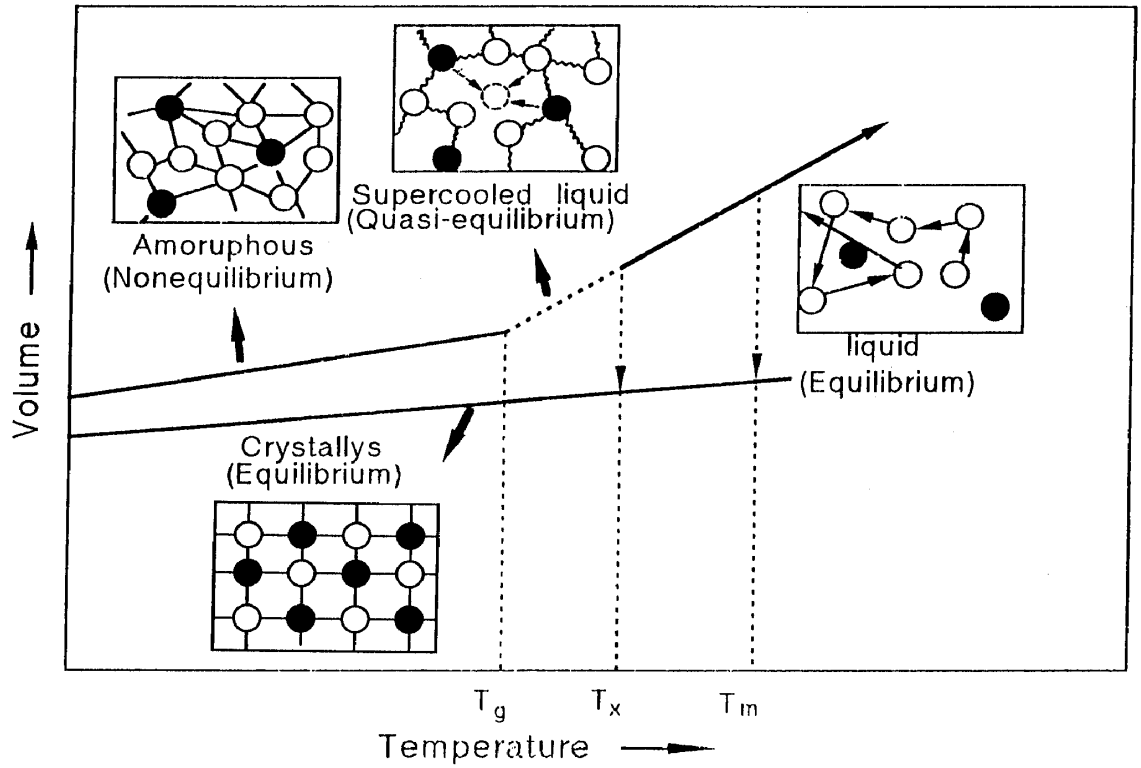

Fig. 1 Schematic illustration of the changes in specific volume and atomic configuration among crystal, liquid, supercooled liquid and glass.

crystallization presents the change from an amorphous solid to a crystalline solid. When the temperature region of the supercooled liquid is defined as $\Delta T_x (=T_x - T_g)$, the ΔT_x value is thought to correspond to the thermal stability of the supercooled liquid.

When the stability of the amorphous alloy is investigated on the basis of thermodynamics, the fundamental concept is just the same between amorphous alloys and oxide glasses. However, the ΔT_x value for oxide glasses is usually above 50 K[6] while no glass transition is observed for a majority of amorphous alloys, though some amorphous alloys in noble-metal base systems as exemplified for Pd-Ni-P and Pt-Ni-P have a large ΔT_x value of about 50 K[7]. In the circumstances, it has been found[2]-[4] that amorphous alloys in La-Al-Ni, Mg-Ni-La and Zr-Al-Ni systems have large ΔT_x values of 60 to 100 K which are comparable to those for oxide glasses. Consequently, the supercooled liquid state for these amorphous alloys is more stable as compared with that for other amorphous alloys and the use of the new amorphous alloys enables us to examine the fundamental properties of the supercooled liquid.

III. Viscosity and Workability of the Supercooled Liquid

The T_g shown in Fig. 1 is defined as the temperature at which the viscosity (η) is of ther order 10^{12} Pa.s and almost all properties change drastically near T_g. For instance, the diffusion of atoms occurs cooperatively in the temperature range above T_g, being different from the diffusion mode in crystalline solids. As a result, the glass transition causes a drastic increase in specific heat, specific volume and electrical resistivity and a drastic decrease in viscosity. These changes can be explained on the basis of the change in free volume.

Figure 2 (a) shows an illustration of free volume in an amorphous solid and the regions marked with dark contrast represent the free volume. It is generally thought[8] that the constituent atoms in the free volume can move without loss of energy. When the constituent elements are frozen by lquid quenching, each element occupies fixed positions and lies in a limited atomic configuration. For instance, the "c" atom in Fig. 2 (a) is surrounded by five atoms and the region in which the "b" atom can move is rather narrow as indicated in the figure, when the repulsive force agianst the neighbor atom is taken into consideration. The distance between the "c" atom and the nearest neighbor atoms is larger than the critical dstance resulting from the interaction between the atoms, leading to an increase in the size of the free volume. Furthermore, since the "a" atom is not restrained

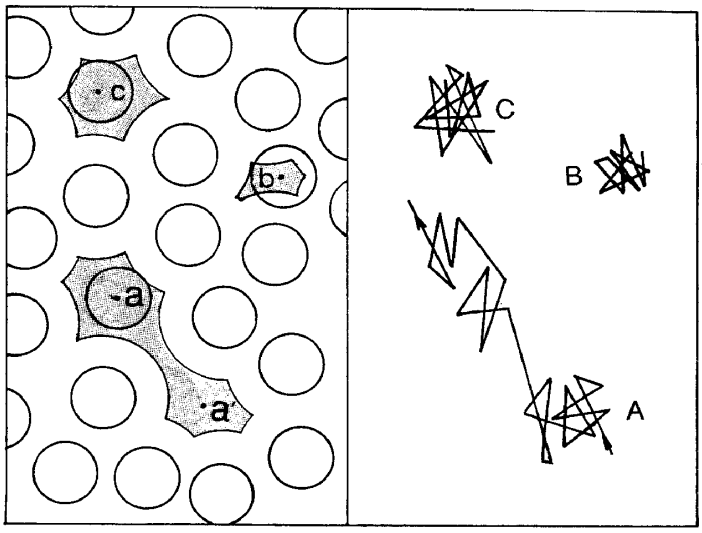

Fig. 2 Schematic illustrations of the existence of free volume including each atom "a", "b" and "c" (a) and the trace of the rearrangement of these atoms (b).

with the surrounding atoms, it is easy for the "a" atom to move to the position of "a'", leading to the rearrangement of and the other atoms to the position "a". Such an atomic rearrangement does not occur for the "b" and "c" atoms. Figure 2 (b) shows the trace of the rearrangement of the "a", "b" and "c" atoms. The rearrangement of the "b" and "c" atoms is due to the usual vibration of atoms in the solid, while the rearrangement of the "a" atom is the same as that of atoms in the liquid. The amount of the free volume (V_f) changes as a function of temperature and increases exponentially with increasing temperature. The number and size of region in which the "a" atom exists increase rapidly in the temperature range above T_g.

It is generally known that the relation between η and V_f is expressed by $\eta \propto \exp(1/V_f)$. This indicates that η decreases exponentially with increasing V_f. Consequently, it is said that η is extremely low in the supercooled liquid with large V_f. Figure 3 (a), (b) and (c) show the temperature dependence of hardness, tensile strength and viscosity, respectively, for an amorphous La-Al-Ni alloy[9]. These properties decrease rapidly near T_g, indicating that the amorphous alloy has a large deformability in the supercooled

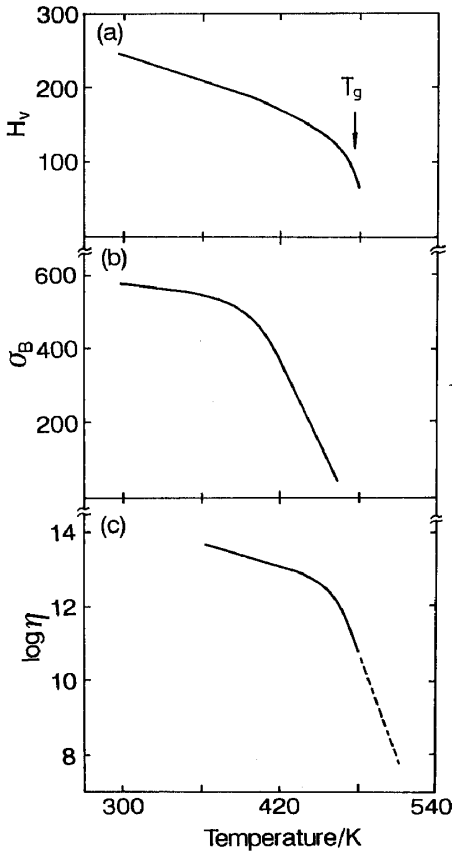

Fig. 3 Vickers hardness (a), tensile fracture strength (b) and viscosity (c) as a function of temperature for an amorphous $La_{55}Al_{25}Ni_{20}$ alloy.

liquid. As shown in Fig. 3 (b), the temperature at which the tensile fracture strength decreases significantly is lower by about 15 K than those for the hardness and viscosity. The difference is presumably due to the influence of the application of tensile load. A similar decrease in T_g by the application of tensile load is also seen for polymer materials.

IV. Production of Amorphous Alloy Balloons

We have previously reported[10] that the $La_{55}Al_{25}Ni_{20}$ amorphous alloy has a wide supercooled liquid region reaching 70 K. It is therefore thought that the stability of the supercooled liquid is rather high for the amorphous alloy. Figure 4 shows the relation between the viscosity and workability for conventional oxide glasses. The glass becomes significantly soft in the η range below $10^{6.6}$ Pa.s, indicating that various working processes can be applied to the glasses. The η value of the present La-Al-Ni amorphous alloy is evaluated to be of the order 10^{6-7} Pa.s at about 510 K from the extrapolation of the temperature dependence of η shown in Fig. 3. It is therefore expected that the amorphous alloy is easily deformed by the pressing, drawing and blowing processes which have presently been used for the working of oxide glasses.

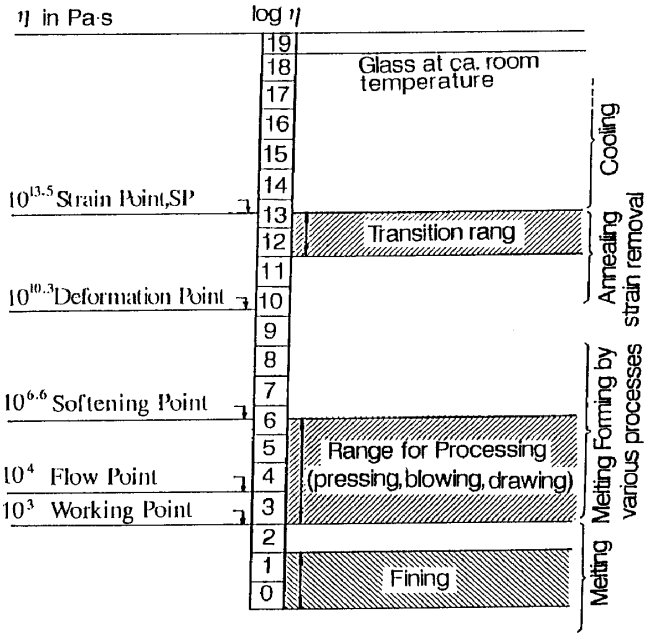

Fig. 4 Correlation between viscosity and workability for glasses.

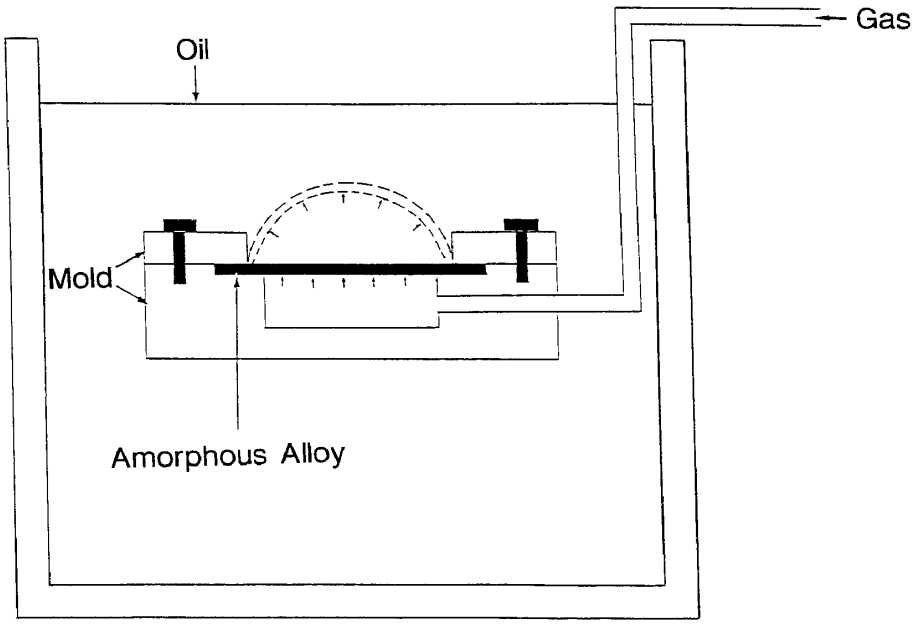

Fig. 5 Schematic diagram of the equipment used for the production of an amorphous alloy balloon.

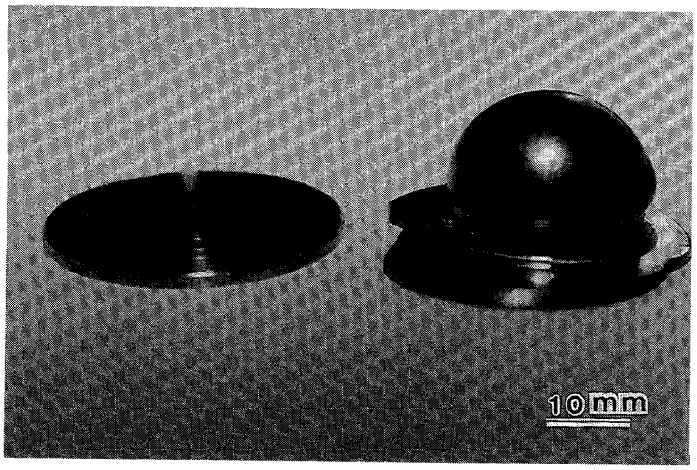

Fig. 6 Photograph revealing the external appearance of an amorphous $La_{55}Al_{25}Ni_{20}$ disk and an amorphous alloy balloon produced by blowing the amorphous disk.

Here, we shall introduce the first example in which an amorphous alloy balloon is formed by the blowing process. The raw material used for the production of the amorphous alloy balloon is an amorphous $La_{55}Al_{25}Ni_{20}$ disk with a diameter of 35 mm and a thickness of 2.2 mm produced by a metallic mold casting process. As illustrated in Fig. 5, the amorphous disk is fixed with the metallic mold by tightening bolts. By connecting the inlet gate for gas with an air pump for bicycle and sending air into the metalloic mold, an air pressure is applied to the central area of the amorphous metallic disk. When the metallic mold is immersed in a silicon oil heated at 510 K, the application of an air pressure of about 0.2 MPa causes a blowing of the central area in the amorphous alloy disk, leading to the formation of a balloon. This blowing process is similar to the blowing for heated glasses by giving out breath. Figure 6 shows the external appearance of the resulting La-Al-Ni amorphous balloon, along with the original amorphous disk. It is seen that the height in the balloon reaches about 30 mm. Even after the severe deformation, the blowed area has a good metallic luster and the thickness of the blowed area still keeps a large value of about 1 mm, presumably because the blowing deformation has occurred very homogeneously through a significant viscous flowability. In addition, a cylindrical hole with

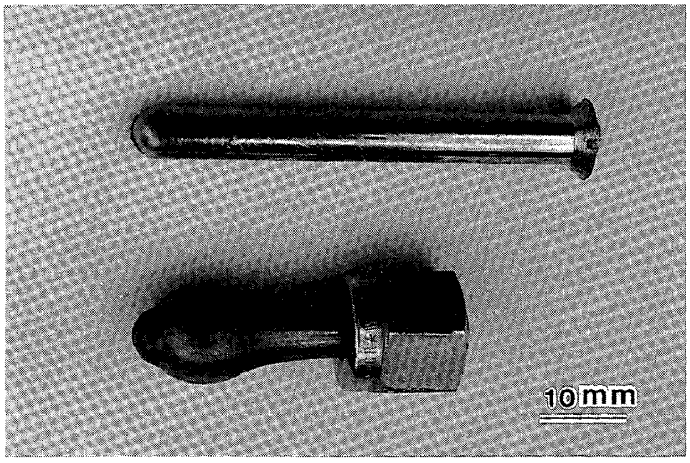

Fig. 7 Photograph revealing the external appearance of amorphous $La_{55}Al_{25}Ni_{20}$ tubes in as-cast and blowed states.

a diameter of about 3 mm is bored in the amorphous cylinder with a diameter of about 6 mm prepared by the metallic mold casting process, as shown in Fig. 7. The application of an air pressure of about 0.2 MPa into the cave immersed in a silicon oil heated at 510 K causes a blowing deformation to a spherical shape only in the heated area.

In addition, the amorphous alloy cylinder was deformed by tensile applied load at 510 K. As a result, the elongation was found to reach as large as about 14000 % because of the large viscous flowability, as exemplified in Fig. 8. It is important to point out that the elongation is much larger than the largest elongation (5000 to 6000 %) due to superplasticity for crystalline materials. Interestingly, the temperature at which the superplasticity appears in conventional crystalline alloys is in the range of $0.6T_m$ to $0.7T_m$, in agreement with the T_g/T_m value (0.6 to 0.7) for the amorphous alloys. However, the strain rate at which crystalline alloys exhibit the superplasticity lies in the range below about 10^{-3}[11]. On the other hand, the large elongation in the supercooled liquid state for the amorphous alloy is obtained at high strain rates above 10^{-2}. In addition, the applied pressure which is required for the appearance of superplasticity in crystalline materials is less than about 0.6 MPa[12] while the applied pressure for the viscous flow of the

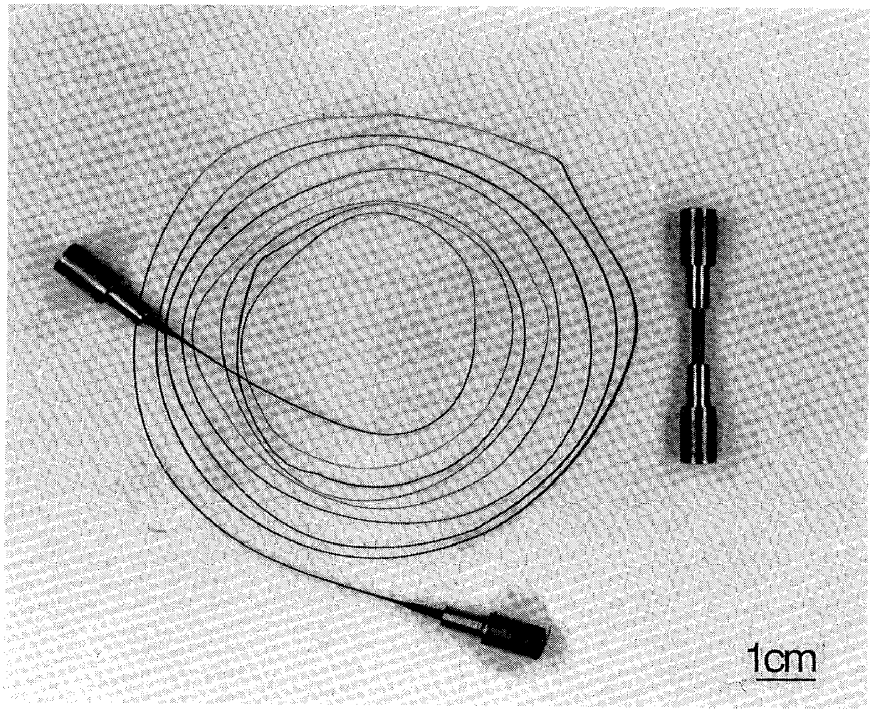

Fig. 8 Photograph revealing the external appearance of an amorphous $La_{55}Al_{25}Ni_{20}$ cylinder and an amorphous alloy wire produced by pulling the amorphous cylinder.

supercooled liquid is as low as below 0.2 MPa. Although the superplatic deformation has been thought to occur mainly through a grain boundary sliding, the detailed mechanism remains unknown. It is interesting to point out that the existence of an amorphous phase along grain boundaries has remained as one of the mechanisms for the superplasticity.

V. Conclusion

The morphology of a large number of amorphous alloys reported up to date is limited to the ribbon form with small thickness because of the limitation resulting from glass-forming ability. Consequently, little has been made about the subsequent working against amorphous alloys, though there are a number of papers on the consolidation of amorphous alloy powders. Recently, we have also found that bulky amorphous alloys form in Mg-based alloy systems as well as in Zr-based alloy systems by the metallic mold casting method and their amorphous alloys exhibit a wide supercooled liquid region before crystallization. Hereafter, there is a high possibility that a similar working process by utilizing the large viscous flowability of the supercooled liquid is also applied to Mg-based amorphous alloys with high specific strengths and can lead to the production of bulky amorphous alloys with various complicated morphologies. These phenomena are expected to attract increasing interest from the viewpoint of materials science and new working processes.

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